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POROUS CERAMICS OBTAINED FROM STRONTIUM ZIRCONATE

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A porous ceramics based on strontium zirconate synthesized from zirconia of grade TsRO-2, baddeleyite powder of grade PB-1, and strontium carbonate with the use of a burning-off additive, namely, bead polystyrene, is described. It is shown that porous zirconate ceramics can be produced by a single-stage process that combines synthesis and sintering. The material was created for lining high-temperature electric furnaces.

Resistive electric furnaces for high-temperature tests of materials are constructed using heating elements fabricated from lanthanum chromite, zirconia, and molybdenum disilicide, which can provide a temperature of 1800 – 2000°C. However, an optimum material has not yet been obtained for lining such furnaces.

It is expedient to study the possibility of fabricating parts of a furnace lining from strontium zirconate, namely, dense articles for the hottest layer and porous articles for subsequent layers. The valuable combination of such properties of strontium zirconate as a high melting temperature (2750°C), high resistivity in the range of 1500 – 2000°C, and chemical stability, especially in an alkaline medium, are good prerequisites for the study.

The greatest difficulties arise in synthesis and sintering of parts from highly refractory zirconates. It is recommended that dense materials from strontium zirconate be fabricated in two stages, namely, preliminary synthesis at 1400°C and subsequent roasting at 1700°C [1], because of the high linear shrinkage in sintering (20 – 25%). The synthesis is also accompanied by an undesirable effect connected with the predominant diffusion of strontium oxide. It can be assumed that in the fabrication of a porous material this effect can be useful because it will compensate the shrinkage. Moreover, in the case of fabrication of a porous refractory the synthesis and the sintering can be combined, which has been tried by us in the present work. Another difficulty in the technology is the creation of a porous and simultaneously strong structure.

In the present work we made an attempt to fabricate a layered heat-insulating refractory whose structure consisted of alternating layers with markedly different porosities. We hoped that the porous layers would provide low heat conduction and the denser layers would provide structural strength for the lining components. The simplest variant from the standpoint of the technology is a two-layer structure with a densely sintered layer in the hottest zone of the lining.

We used strontium carbonate of grade Ch (TU 6-09-4165–84) as the strontium-bearing component and zirconia of grade TsRO-2 (GOST 21907–76) and a baddeleyite powder of grade PB-1 produced by the Kovdorskii mining and dressing works (TU 48-0572-17-252–91) as the zirconium-bearing component.

Although the purer chemical reagent TsRO-2 should obviously provide better properties in the synthesized zirconate, the baddeleyite powder is of interest as a less expensive and accessible substance for refractory production. In contrast to the initial powders of strontium carbonate and zirconia that possess a grain size suitable for the synthesis (predominantly less than 3 μm) the baddeleyite powder has comparatively coarse grains (Fig. 1) and has to be crushed spe-

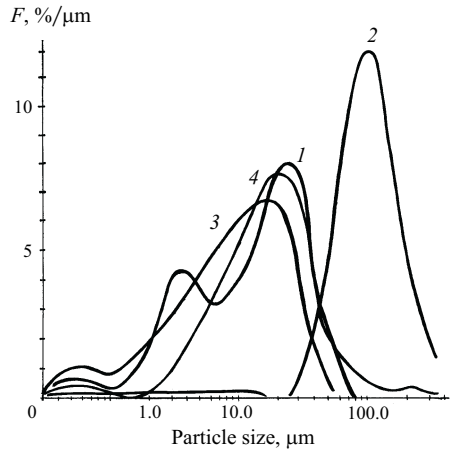

Fig. 1. Curves describing the size distribution of the powder particles: *1*) initial zirconia of grade TsRO-2; *2* and *3*) baddeleyite powder of grade PB-1 before and after milling, respectively; *4*) strontium zirconate synthesized with the use of TsRO-2 reagent (after wet milling).

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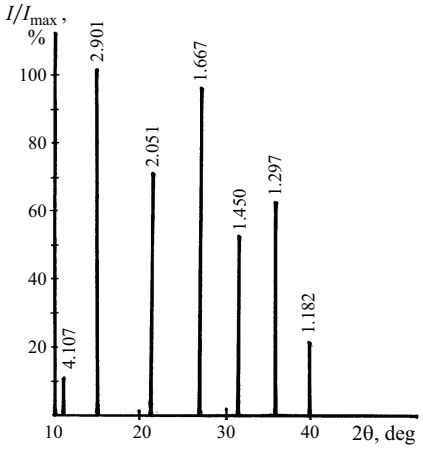

Fig. 2. X-ray diffraction diagram of strontium zirconate with the use of TsRO-2 reagent.

cially. We used vibration crushing to reduce the grain size of the PB-1 powder to the needed value.

The reagents taken in a stoichiometric proportion were mixed in a dry state in a plastic mixer. The mixture obtained was roasted in corundum containers at 1400 – 1700°C. In the case of the two-stage process the synthesized strontium zirconate was subjected to wet milling.

The material for the densely sintered layers of the refractory was shaped by pressing in steel molds at a pressure of 100 MPa, and the layers with a different porosity were shaped by ramming. The porous structure was created and controlled by introducing preliminarily foamed polystyrene granules with different bulk densities (0.06 – 0.20 g/cm^3) as a burning-off additive [2].

The roasting was performed in a furnace with heating elements fabricated from lanthanum chromite of type ÉKhK at a temperature of 1700°C.

The synthesis of strontium zirconate occurred in the entire temperature range. We did not detect the original oxides of zirconium and strontium within the sensitivity of an x-ray phase analysis performed in an ionization diffractometer and repeated in a more precise installation with a Guinier chamber, which was interpreted as an indication that the synthesis of strontium zirconate had completely finished (Fig. 2).

The microstructure of the dense and porous materials determined with the help of a scanning electron microscope on a fresh fracture surface is presented in Figs. 3 and 4.

The densely sintered material has a fine-grained structure with individual fine pores 1 – 2 μm in size (see Fig. 3*a*). The matrix is formed by sintered well-shaped grains (see Fig. 3*b*).

In accordance with the classification of [3] the porous materials have the structure of a cellular ceramics with a sintered skeleton. They have dense or low-porosity sintered bridges and pores that are coarse and spherical with a diameter of 1 – 2 mm due to the burning-off of the polystyrene grains (see Fig. 4*a* and *c*) and fine channel pores less than 5 μm in diameter due to the migration of gases emitted in the burning process. The open porosity is 42 – 48%. The surface

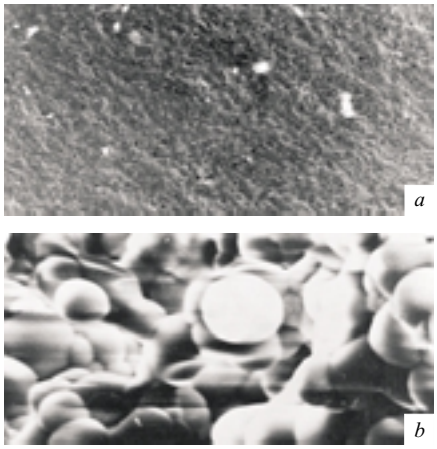

Fig. 3. Microstructure of a densely sintered specimen of strontium zirconate: *a*) overall view (× 350); *b*) matrix (× 5000).

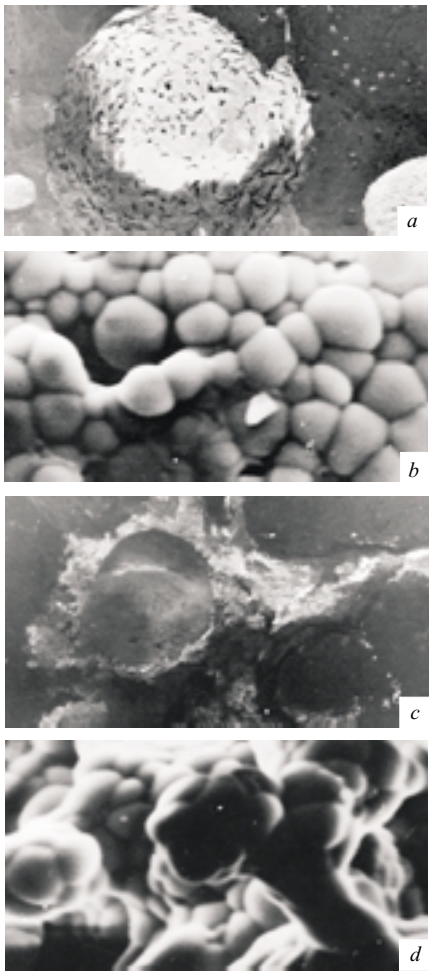

Fig. 4. Microstructure of a porous strontium zirconate ceramics obtained by two-stage (*a*, *b*) and one-stage (*c*, *d*) processes: *a*, *c*) overall view of a pore (× 35); *b* and *d*) pore wall (× 3500 and × 7500, respectively).

of the pores is very rough. The structure of the pore walls is identical to the general structure of a densely sintered material. The pore walls are formed by round pores grown together (see Fig. 4*b* and *d*).

The porous materials fabricated by the one-stage and two-stage processes have quite similar structures. It is noteworthy that after a high-temperature creep test at 1650°C the structure remains unchanged, which indicates that its formation has finished in the roasting process.

The apparent density and the open porosity of the dense and the porous material turned out to be equal to 5.24 and 2.74 g/cm^3 and 0.28 and 47.8%, respectively. At the same time, their linear shrinkages in roasting differed little and amounted to 12 – 18 and 21 – 28%, respectively. The extra linear shrinkage of specimens of both kinds at 1700°C with a hold of 2 h was 1%.

The temperature of deformation under a load of 0.05 MPa for the porous refractory fabricated in two stages was studied by the method of ISO 1893 and in an installation created at the D. I. Mendeleev Russian Chemical Technological University. As a result of tests of porous specimens of strontium zirconate synthesized at temperatures of 1420 and 1500°C and roasted at 1700°C we established the following: the temperature of 0.5% deformation was 1410 and 1460°C, the temperature of 1% deformation was 1520 and 1530°C, and the temperature of 2% deformation was 1610 and 1620°C (Fig. 5).

The thermal conductivity of the porous refractory fabricated in two stages was studied in accordance with ISO 8894-1 and by the "hot wire" method in another installation created at the D. I. Mendeleev Russian Chemical Technological University. The dependence of the thermal conductivity of a specimen with an open porosity of 47.8% is presented in Fig. 6. It can be seen that the thermal conductivity in the studied temperature range (700 – 1000°C) increases. This can be connected with the increase in the contribution of the radiative component of heat conduction to the "effective heat conduction" [4].

We used the results of the present study to fabricate specimens of a two-layer refractory where the densely sintered and porous layers were created separately and then glued by slip of the same composition. In the production of the porous layer we combined successfully the synthesis and the sintering and used both TsRO-2 and PB-1 powders. A comparison of the results of the traditional two-stage (separate) technology of zirconium-bearing ceramics and the one-stage process showed that the shrinkage in the one-stage process was half that in the two-stage one.

Thus, we have obtained a porous heat-insulating material from strontium zirconate by the method of burning-off additive that can be used for parts of a lining or in the form of a two-layer refractory in combination with a densely sintered layer. Pilot specimens were fabricated for a furnace with heaters made of lanthanum chromite.

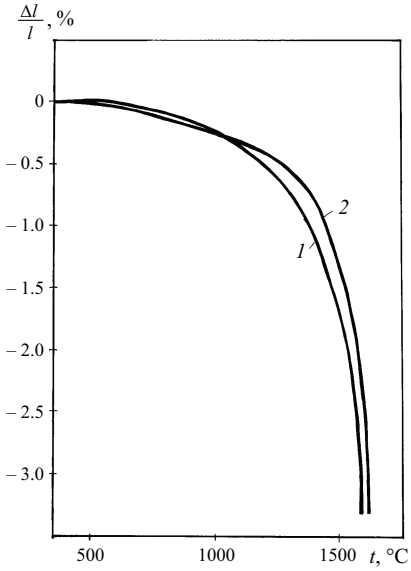

Fig. 5. Deformation under a load upon heating specimens of strontium zirconate synthesized at temperatures of 1420°C (*1*) and 1500°C (*2*).

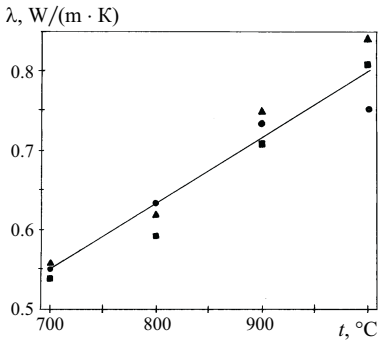

Fig. 6. Temperature dependence of the thermal conductivity of a porous specimen of strontium zirconate.

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